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A modelling framework to simulate river flow and pesticide loss via preferential flow at the catchment scale

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Abstract

A modelling framework with field-scale models including the preferential flow model MACRO was developed to simulate transport of six contrasting herbicides in a 650 km^2 catchment in eastern England. The catchment scale model SPIDER was also used for comparison. The catchment system was successfully simulated as the sum of multiple field-scale processes with little impact of in-stream processes on simulations. Preferential flow was predicted to be the main driver of pesticide transport in the catchment. A satisfactory simulation of the flow was achieved (Nash-Sutcliffe model efficiencies of 0.56 and 0.34 for MACRO and SPIDER, respectively) but differences between pesticide simulations were observed due to uncertainties in pesticide properties and application details. Uncertainty analyses were carried out to assess input parameters reported as sensitive including pesticide sorption, degradation and application dates; their impact on simulations was chemical-specific. The simulation of pesticide concentrations in the river during low flow periods was very sensitive to uncertainty from rain gauge measurements and the estimation of evapotranspiration.

Highlights

- The catchment system can be simulated as the sum of multiple field-scale processes
- Pesticide concentrations in stream flow were driven by field-scale processes
- In-stream processes had little effect on simulations
- Uncertainties in rain gauge recording affected the simulation of low-flow periods
- SPIDER simulates important lateral flow losses that can occur when drains are not flowing

Keywords: Pesticide; preferential flow; MACRO; SPIDER; in-stream; catchment

1 Introduction

Modelling the fate of pesticides at the catchment-scale is an important tool for pesticide management to gain insight into behaviour at this scale and to evaluate the impact of different management

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practices. Pesticide loss through subsurface drainage (when tile drains are present) is a dominant route for pesticide transport to surface waters with surface runoff also locally important (Harris and Catt, 1999; Johnson et al., 1996). Heavy clay soils with artificial drainage frequently exhibit pesticide transport via preferential flow, causing surface water contamination (Brown et al., 1995; Johnson et al., 1996).

The model of water flow and solute transport in macroporous soil, MACRO (Jarvis et al., 1991), is the most widely used preferential flow model at the field scale in Europe. A few studies have applied field-scale models in catchment modelling by considering that the fate of pesticides in the catchment would be the result of the sum of multiple field-scale processes (Lindahl et al., 2005; Tediosi et al., 2013). Monitoring studies of diffuse water pollution by pesticides at different hydrological scales have shown that pesticide losses normally occur as pulses of fluctuating concentrations with similarities in their pattern; thus, patterns (but not magnitude) of concentrations measured in a small receiving water body adjacent to an arable field are broadly conserved in terms of the timing and duration of peaks when the same pesticide is monitored further downstream (Brock et al., 2010). These patterns of peak concentrations are largely dependent on rainfall behaviour, suggesting that processes occurring within the river network may not be a major influence on the timing and magnitude of peak pesticide concentrations in surface waters at larger scales.

Coupling fate models involves combining more than one model in order to establish a modelling framework that can simulate a broader system than can any of the component models in isolation (Zhu et al., 2013). In this paper a modelling framework was developed by combining hydrological and fate models in an attempt to simulate various pathways of water flow and their associated pesticide losses in the Wensum catchment in the eastern region of the UK. The Wensum is one of the six priority catchments in England and Wales targeted under the Catchment Sensitive Farming programme (CSF), to reduce diffuse water pollution by pesticides. Regular pesticide monitoring has been undertaken since 2006 to evaluate the effectiveness of the management actions. The modelling framework using MACRO aimed to test whether the catchment system can be simulated as the sum of multiple field-scale processes.

The catchment scale model SPIDER is a preferential flow model that simulates hydrological flow and pesticide fate in small catchments (Renaud et al., 2008). In contrast to field-scale models like MACRO, SPIDER considers spatial variability of soils, crops and pesticide usage in the catchment to simulate the effect of the transport and sorption of pesticides in the river network. SPIDER was also applied to the Wensum to compare results from a catchment model to the modelling framework using a field-scale model.

Despite the importance of uncertainty analyses, very few pesticide modelling studies include them in their results. Physically-based hydrological and pesticide transport models require a large amount of input data from the study area that are not always known with certainty (Sohrabi et al., 2002). Depending on the level of accuracy needed and the sensitivity of the model, parameters can be left at their default values, taken from databases, derived from empirical equations or estimated using expert judgment; any of these procedures will introduce uncertainty into the model, in addition to the simplification of the physics and processes by a model conceptualisation (Dubus et al., 2003). These uncertainties are responsible for reducing the predictive capacity of the simulation, providing results that differ from reality. In addition, different sources of uncertainty can magnify the overall uncertainty of the outputs (Zhang et al., 1993). An uncertainty analysis of key sources of uncertainty in the input parameters was also included to assess their impact on model simulations.

2 Methods

2.1 Site description and data acquisition

The Wensum catchment is located in the eastern region of the UK, to the north west of Norwich and covers an area of approximately 650 km^2. The River Wensum flows approximately 78 km through the county of Norfolk from Colkirk Heath to its confluence with the River Yare in Norwich (Figure 1). The monitoring point located at Sweet Briar Road Bridge (National Grid Reference: TG 206 095) defined the simulated catchment. Slowly permeable soils with tile drainage systems located on the river valley (Beccles and Burlingham associations) constitute the main soils in the catchment (Hodge et al., 1984), accounting for 57% of the catchment area. At the top of the catchment, the soils are a combination of well-drained loamy soils (Barrow) with patches of sandy soils (Newport), whilst the Newport association predominates at the base of the catchment. The floodplains are dominated by peaty soils (Adventurers) and loamy and sandy soils with naturally high groundwater and peaty surface layers (Isleham). Meteorological data from the closest stations to the catchment were used including Norwich Airport (hourly rainfall), Wattisham (hourly solar radiation and daily maximum and minimum temperature) and Marham (hourly wind speed and vapour pressure) (Figure A–1).

Physicochemical properties of the pesticides used in the models were taken from typical values reported in the literature (Table A–1). Reported mean values of the soil-water partition coefficient normalised to soil organic carbon content (K_{oc}) were used in the model; the exception was for propyzamide where the reported K_{oc} was very large (840 ml g^{-1}). Pedersen et al. (1995) reported soil-water partition coefficient (K_d) values for various soils with different organic carbon contents. Based on the organic carbon content of Beccles (1.7%) and Burlingham (1.4%), K_d values of 4.96 and 4.09 ml g^{-1}, respectively, were estimated by extrapolation of the reported data. These K_d values correspond to an average K_{oc} value of 292 ml g^{-1} that was then used in the model to improve the simulation of propyzamide.

The simulated crops were winter wheat (WW) and oilseed rape (OSR) as they are the main crops present in the catchment and all of the pesticides simulated are applied to one or both crops. Generic crop parameters were taken from FOCUS (2000) Châteaudun scenario, except for dates of growth stages for WW which were modified to agree with typical growing information for the UK. Crop areas (Table A–2) and pesticide usage (Table A–3) reported biannually by crop and pesticide type as the total area treated with pesticide (in ha) and total pesticide weight applied (in kg) for the Eastern region were used to determine the proportion of crop area treated with pesticides and the application rates by assuming that the usage in the catchment would match that in the region. Dilution from untreated areas was implicitly included by calculating average application rates for the whole catchment for each of the pesticides simulated.

Measured data on water flow and pesticide concentrations in the River Wensum used for the model evaluation were supplied by the Environment Agency of England and Wales. Water flow was measured at the gauging station at Sweet Briar Bridge with 15-minute resolution and reported as daily mean flow. The frequency of water samples collected for pesticide analysis varied during the year but was usually twice a week (CSF, 2012). Grab water samples were also collected at Sweet Briar Road Bridge and sent for analysis by the UK National Laboratory Service using accredited methods developed to analyse suites of pesticides in natural waters. Table A–4 shows the limit of quantification for each pesticide as these changed during the studied period.

2.2 MACRO model parameterization

MACRO is a one-dimensional physically-based model of water flow and solute transport that divides the soil porosity into two flow domains, micropores and macropores. A full description of the governing equations and the model parameters has been given elsewhere (Jarvis et al., 1991). MACRO 5.2 was used to simulate water flow and pesticide loss through deep percolation and tile drainage. A modelling framework using MACRO was developed to simulate river flow in the Wensum which included a groundwater mixing model to simulate the baseflow behaviour of the river and to allow leaching water and pesticide in the saturated zone to mix before being routed to the river.

Urban areas are reported to account for approximately 2% of the Wensum catchment (Sear et al., 2006); however, this information refers to major urban areas, not taking into account roads, farms and small villages. For modelling purposes it was estimated that the total developed (constructed) areas would be about 4% of the catchment. In the model, it is considered that 50% of the rainfall from hard surfaces will enter the river network as rapid runoff. Surface runoff was the only source of flow considered from the developed areas.

Comparison of river flow with modelling using RZWQM (Ma et al., 2004) and PRZM (Carsel et al., 1985) suggested that surface runoff from arable land was not a significant process in the catchment, so neither model was included in the framework (Villamizar, 2014). Other inflow and outflow sources (such as water abstraction, irrigation and sewage discharge) were assumed to have little impact on the hydrograph. Modelling results for the different pathways of water flow were scaled-up to the entire catchment using an area-weighted average approach based on soil type. The conceptual scheme in Figure 2a) summarises this strategy. Travel time was ignored, assuming that there is no delay (larger than a day) between flow leaving the field and arriving at the catchment outlet.

An important aspect of flow estimation is the calculation and incorporation of the baseflow component of the hydrograph. Baseflow is primarily generated from groundwater discharge into the river network which depends on regional hydrological conditions. A simple groundwater mixing model was developed to simulate the baseflow in the Wensum catchment and the transfer of pesticide that could reach the groundwater by leaching. The groundwater mixing model, implemented via a spreadsheet calculation, performs a simple mass balance of water flow and pesticide mass at a daily time step (Figure 2b and Equation 1). Input data are the simulated inflow volume of deep water recharge ($V_{i,t}$ in m^3) and pesticide leaching mass that reaches the groundwater ($m_{i,t}$ in mg), predicted by MACRO at a daily time-step ($t \geq 1\ day$). The aquifer is represented as a mixing tank (T) with the same base area as the catchment. The daily volume of water ($V_{T,t}$), pesticide mass ($m_{T,t}$) and concentration ($C_{T,t}$) in the aquifer are also calculated on a daily basis (in m^3, mg and mg m^{-3}, respectively). The outputs (o) from the model are the volume of water ($V_{o,t}$), pesticide mass ($m_{o,t}$) and concentration ($C_{o,t}$) outflow (in m^3, mg and mg m^{-3}, respectively) moving from the groundwater (or tank) to the river at the rate of the outflow factor, OF, which was set at a constant value. The outflow factor and the initial tank volume ($V_{T,1}$) were set by manual trial-and-error calibration against Nash-Sutcliffe model efficiency coefficients plus visual comparison to match measured flow during periods dominated by baseflow and the flow at the beginning of the simulation, respectively. Pesticide degradation and sorption in the saturated groundwater zone are assumed to be negligible within the model.

$$Inflow\ (i)\ \ V_{i,t}; m_{i,t}$$

$$Tank\ (T)\begin{cases} V_{T,t};\quad m_{T,t} = m_{i,t};\ C_{T,t} = m_{T,t} / V_{T,t}, & if\ t = 1 \\ V_{T,t} = V_{T,t-1} - V_{o,t-1} + V_{i,t};\ m_{T,t} = m_{T,t-1} - m_{o,t-1} + m_{i,t};\ C_{T,t} = m_{T,t} / V_{T,t}, & if\ t > 1 \end{cases} \qquad (1)$$

$$Outflow\ (o)\quad V_{o,t} = \left(V_{T,t} + V_{i,t}\right) \times OF;\quad m_{o,t} = C_{T,t} \times V_{o,t}$$

Soil profiles for each simulation were divided into 60 layers. The only soils requiring tile drainage systems were Beccles and Burlingham. Initial moisture content in the different horizons at the start of the simulations was set to field capacity. A constant hydraulic gradient was used as the bottom boundary condition in the model. Input values were established from a combination of guidance on how to parameterise MACRO (Beulke et al., 2002; FOCUS, 2000) as follows: the boundary water tension between micropores and macropores (CTEN) for each horizon was selected from suggested values based on clay content. Then, their respective water content values (XMPOR) were derived from water release curves measured on intact cores in the laboratory (water content at zero suction) (Hallett et al., 1995) by interpolation between the two points of the water release curve closest to CTEN; the boundary conductivity (KSM) was calculated from CTEN and XMPOR using the equation proposed by Laliberte et al. (1968) and Jarvis et al. (1997) and the pore size distribution factor for macropores (ZN) was initially established by expert judgement and then adjusted by model calibration.

Only very limited calibration of crop and soil parameters was carried out to improve the simulation of the flow recovery at the end of low-flow periods. Maximum root length was decreased to reduce soil water extraction from deeper layers. Soil parameters for Beccles and Burlingham were calibrated to increase water infiltration capacity by facilitating the movement of water in the soil profile. The modified parameters were the tortuosity/pore size distribution factor for macropores (ZN) and the effective diffusion path length (ASCALE). ZN was reduced by 1.0 for all horizons in Beccles and by 0.5 for the first two horizons in Burlingham. For Burlingham, ASCALE was increased to 10 for the first horizon since the original value of 5 was relatively small (common values range between 10 and 40). ZN is a sensitive parameter that influences preferential flow and cannot be measured directly; hence, systematic calibration is normally required (Beulke et al., 2002).

2.3 SPIDER model parameterization

The preferential flow model SPIDER simulates pesticide loss into surface water from the most important routes of pesticide entry which are spray drift, drainflow, surface runoff and lateral flow (lateral transport within the soil profile); a detailed description of the model is presented by Renaud et al. (2008). The catchment is described in the model as a series of land blocks (with similar soil and land use) and stream reaches interconnected according to the possible pesticide entry pathways which may be specified by the user. The model enables representation of the spatial variability of the catchment. In order to simulate pesticide transport in the soil profile in SPIDER, the soil porosity is divided into two pore domains (macropores and micropores). This is a similar approach to MACRO, but simplified to enable a reasonable simulation time at an hourly resolution at the catchment scale, and also to simplify the parameterisation process. Then, vertical and lateral movement of water is triggered by soil moisture exceeding field capacity. The water balance (mm for θ, and mm h^{-1} for all other terms) at an hourly time step t is calculated from Equation 2:

$$\theta_t = \theta_{t-1} + R_{soil,t} + Ir_t - ETa_t - P_t - LM_t - D_t - Ru_t \qquad (2)$$

where θ is the soil water content, R_{soil} and Ir are the amount of rainfall and irrigation, respectively, ETa is actual evapotranspiration, P is percolation through the soil profile, LM is lateral flow, D is drainage via tile systems, and Ru is surface runoff (Renaud et al., 2008). Daily reference evapotranspiration (ETr) is first calculated with the FAO Penman-Monteith equation; then hourly ETr values are assumed to be the same for each hourly interval during daylight hours and hourly ETa is calculated from the crop and water stress coefficients following Allen (1998). Percolation above any drained soil layer is calculated to include preferential flow where soil wetness exceeds a threshold water tension at which macropore flow is initiated. Loss of water from the base of the profile is controlled by a groundwater recharge value in the deepest layer of the soil profile specified by the model user. If soil water content after percolation is greater than soil water at field capacity, excess water can be removed as lateral flow for layers above the bottom elevation of a reach. Lateral flow is described by the kinematic storage model of Sloan and Moore (1984) using the lateral hydraulic conductivity, flow velocity, soil depth, slope angle and field length. Drainage is generated in the model when the layer below the drained horizon is saturated and the soil water content is greater than the field capacity in the drained horizon, or when the water table reaches the drained horizon. Surface runoff is simulated when rainfall intensity exceeds the saturated hydraulic conductivity of the soil or when rain falls on an already saturated soil.

The general equation of the soil pesticide balance to calculate the pesticide load (mg for $PestL$ and mg h^{-1} for all other terms) at an hourly time step t for each layer is given by Equation 3.

$$PestL_t = PestL_{t-1} + IL_t + PL_t - SDL_t - RL_t - DrL_t - LFL_t \qquad (3)$$

where $PestL$ is the pesticide load in the layer, IL is the load from either application or a layer above, PL is load from percolation, SDL is the pesticide degraded in the soil, RL is the load from runoff, DrL is load from drainage, and LFL is load from lateral flow. Any pesticide transferred from a field into a stream reach is then transported with water flow into consecutive segments up to the catchment outlet. Water flow is routed using the Muskingum method. Pesticide mass balance in stream reaches accounts for pesticide inputs from land blocks, pesticide sorption to stream sediments, degradation, losses by percolation and transport to the next stream reach (Renaud et al., 2008).

The Wensum catchment was described in SPIDER by dividing the river network into 24 stream reaches and the catchment area into 44 land blocks according to their soil association and their location relative to the river sections (Figure A–2). The assumption of relatively homogeneous conditions within these landscape elements is a prerequisite for the approach. Water lost as recharge was used as input to the groundwater mixing model to include the baseflow component of the hydrograph. The saturated vertical and lateral hydraulic conductivities of the soil as well as the hydraulic conductivity at field capacity were set to be calculated by the pedotransfer functions in SPIDER (Evans et al., 1999). The saturated hydraulic conductivity of the sediment layer was 0.5 mm/h and the sediment bulk density, 0.8 g/cm^3. Effective sediment thickness for interaction with pesticide was initially set to 3 mm but then was calibrated to a value of 1 mm to reduce total pesticide sorption to the sediment. Apart from pesticide degradation in the soil, SPIDER also simulates degradation in the river network so degradation values in water and sediment must be supplied to the model (Table A–5).

Model calibration was applied to SPIDER in order to improve the simulation of the water flow by adjusting the water balance to increase the predicted flow in the river network (i.e. increasing percolation and drainflow volumes and reducing evapotranspiration). Evapotranspiration coefficients for all crops were reduced taking into account winter conditions in the Wensum which is prone to freezing during this period. The new values were selected according to ranges reported by Allen (1998).

2.4 Model evaluation

Modelling results were evaluated using visual comparison against the observed flow and pesticide concentrations and from calculation of the Nash-Sutcliffe model efficiency coefficients (NSE; (Nash and Sutcliffe, 1970). NSE values for the simulated flow were calculated on a daily and average daily time-step (t) for MACRO and SPIDER, respectively for each hydrological year (September 1st to August 31st) using Equation 4.

$$\boldsymbol{NSE = 1 - \frac{\sum_{t=1}^{T}\left(Q_o^t - Q_m^t\right)^2}{\sum_{t=1}^{T}\left(Q_o^t - \bar{Q}_o\right)^2}} \qquad (4)$$

where Q_o^t and Q_m^t are the observed and modelled flow at time t, respectively; and $\bar{Q}_o$is the observed mean value. NSE values can range from -∞ to 1. An efficiency of NSE = 1 corresponds to a perfect match between the model and the observed data. A model efficiency of NSE = 0 indicates that the simulation is as accurate as the mean of the observed data, whereas simulations with NSE <0 occur when the observed mean is a better predictor than the model. Therefore, the best simulation results would have positive efficiency values near to one.

Comparisons between pesticide results were carried out on the simulated loads and maximum concentrations for each hydrological year (matching a crop year running September 1 – August 31) during the simulation period (2007-2011). The observed pesticide load was calculated from the daily measured pesticide concentration and water flow using Equation 5 when the concentration was above the LOQ.

$$PestL = Q \cdot PestC \cdot 10^{-6} \qquad (5)$$

where *PestL* is the daily pesticide load in kg, Q is the daily water flow in m^3 and *PestC* is the measured daily pesticide concentration in $\mu g\ l^{-1}$ multiplied by a conversion factor of 10^{-6}. Daily simulated loads were first calculated and then added together to estimate the annual simulated load from SPIDER and MACRO for each crop year for the period 2007-2011.

Additional assumptions were made to calculate pesticide loads on days when the pesticide concentration was reported to be below the limit of quantification (LOQ). A limit value of 0.001 $\mu g\ l^{-1}$ was used to define the minimum pesticide concentration that was taken into account for the calculations. This value is set as the smallest of the LOQ reported for the studied pesticides (Table A–4). Then, the assumptions made for calculating the loads for these days were:

1) For days when the models (SPIDER or MACRO) simulated a pesticide concentration below a value of 0.001 $\mu g\ l^{-1}$, the measured and the simulated concentrations were assumed to be zero. It was considered that if pesticide was neither detected in the sample nor simulated by the models, it is very unlikely that pesticide was actually present in the water.
2) For days when either of the models simulated a concentration above 0.001 $\mu g\ l^{-1}$, the measured concentration was (arbitrarily) assumed to be 25% of the LOQ. This means that if one of the models predicts a pesticide concentration above the set limit of 0.001 $\mu g\ l^{-1}$ but it is not analytically quantified in the samples, there is reasonable probability that the pesticide was present in the water at a concentration smaller than the LOQ.

2.5 Uncertainty analysis

Model performance in the simulation of pesticide concentrations can be affected by several sources of uncertainty in the input parameters in addition to the simplification of the physical description and processes inherent to the model (structural error), the spatial scale and the temporal discretisation applied in the simulations. The influence of uncertainties on model results varies depending on the sensitivity of the parameters; higher uncertainties on the most sensitive parameters would generate a greater impact on the accuracy of the simulation. Sensitivity analysis of pesticide fate models including SPIDER and MACRO have shown that simulations are greatly influenced by the quality and adequacy of precipitation data (Dubus and Brown, 2002; Renaud and Brown, 2008), pesticide sorption and degradation parameters (Dubus and Brown, 2002) and pesticide usage details, particularly application dates (Boithias et al., 2014; Holvoet et al., 2005).

For many years, the UK Meteorological Office (2010) has used the tipping-bucket rain gauge for the automatic recording of rainfall. Uncertainties from tipping-bucket gauges depend mainly on precipitation intensity and timescale (Ciach, 2003; Wang et al., 2008). Ciach (2003) estimated errors in rainfall data using tipping-bucket rain gauges for different timescales applying non-parametric regression tools; a standard error of 10% was obtained for hourly recordings and rainfall intensities similar to those observed at Norwich Airport. The effect of this uncertainty in model input was investigated by running simulations with consistently ±10% of the measured hourly rainfall data.

Although, there are typical application dates reported for pesticides, actual application can vary depending on several factors such as the weather, recommendations on pesticide application and different crop types that the product can be applied to (Gericke et al., 2010). Actual information on pesticide usage in large catchments is seldom available and is difficult to obtain (Boithias et al., 2014; Dubus et al., 2003). An uncertainty analysis into the effect of the use of typical application dates in the model was undertaken for five of the six pesticides; the exception was MCPA since the observed emissions mainly occurred during summer periods when very little or no drain flow was simulated by both models. Carbetamide and propyzamide are post-emergence herbicides with residual action usually applied to OSR between the middle of October and the end of February. The recommendation is not to apply if heavy rain is expected within 48 hours and if drains are flowing or are about to flow. Assuming that farmers had followed these recommendations, SPIDER and MACRO were run varying the application date in intervals of 5 days by analysing the rainfall patterns during the crop season. Simulations for chlorotoluron and mecoprop, herbicides mostly applied on cereals during the autumn-winter period, were run between late October and November with 5-day intervals. Clopyralid is a herbicide with a variety of uses in crops and grassland usually applied during the spring. Simulations for this pesticide were run with a combination of two application dates from late February to early March together with an application in May.

The effect on pesticide simulations due to uncertainties in the use of average reported pesticide sorption and degradation values was evaluated by running different simulations for four of the six pesticides and comparing with the original simulation. The selection criteria for inclusion was availability of average and range in sorption and degradation values from regulatory studies within the pesticide properties database (PPDB) (Lewis et al., 2015). An evaluation of extreme parameter combinations was carried out for each compound by running four simulations combining maximum and minimum K_{oc} and degradation half-life (DT_{50}) values (Table A–1).

3 Results

3.1 Simulation of water flow

The uncalibrated simulations from both models showed under-estimation of the flow for all hydrological years (Table 1 and Figure A–3). After calibration the flow increased significantly for all hydrological years and a good match of the flow was obtained for the year 2009/10 using MACRO. In general, MACRO was closer in the simulation of the observed water flow than SPIDER. For both models, 2008/09 was the hydrological year with greatest under-estimation of the flow; this year was the driest of the four simulated (Table 1). The calibrated hydrographs are compared to the observed flow in Figure 3. Both models showed good simulation of the pattern of water flow. However, both models over-estimated flow during periods of greatest flow and under-estimated flow during periods of low flow. The level of under-estimation throughout the simulation was a more significant issue than over-estimation, particularly during low-flow periods. A better simulation of the recession periods was achieved for MACRO while the simulated flow from SPIDER was significantly smaller than the observed flow. In contrast, during periods of flow recovery (i.e. at the end of low-flow periods) SPIDER matched the timing of increase in flow much better than MACRO.

No surface runoff was predicted by the models for the Wensum primarily due to the efficiency of the tile drainage system. From this result, it was expected that surface runoff generated from arable land would be small. Both models achieved positive model efficiency values for all hydrological years; however, best NSE values were generally achieved for MACRO. A comparison of the actual evapotranspiration calculated by the two models (Figure A–4) showed that for MACRO was 10.1% larger than that for SPIDER over the simulation period. This difference in evapotranspiration is very evident particularly during the summer periods for MACRO which reduces soil moisture content and prevents the soil from wetting up as rapidly as for SPIDER.

3.2 Pesticide concentrations

Comparisons between simulated and measured pesticide concentrations are presented for chlorotoluron, carbetamide and clopyralid in Figure 4 and for mecoprop, propyzamide and MCPA in Figure A–5. Most of the pesticide simulations showed that the models were able to simulate the overall pattern, though not the exact magnitude and timing, of pesticide concentrations at the catchment outlet. The exception was for pesticides applied during spring and summer periods such as clopyralid (Figure 4Figure 4c) and MCPA (Figure A–5c) where large disagreement was observed between simulations and the measured concentrations. Table A–5 compares measured and simulated values for load and maximum concentration in each hydrological year for all pesticides.

Both models achieved a relatively good simulations of the overall pattern of pesticide concentrations for chlorotoluron (Figure 4a). Some differences were observed between simulations. SPIDER predicted peaks earlier than MACRO with first presence in water generally simulated from November and December for SPIDER and MACRO, respectively. MACRO tended to over-estimate concentrations for most of the years by up to one order of magnitude whereas SPIDER had a better match in timing and magnitude of the peaks for most of the hydrological years; the exception was for 2008/09 where SPIDER under-estimated pesticide concentrations by up to a factor of six.

For carbetamide (Figure 4b), both models under-estimated concentrations by similar amounts. SPIDER again simulated water contamination earlier in the winter than MACRO. Better simulations for carbetamide were observed using SPIDER than MACRO, especially in 2010/11 where a good match in the pattern and timing of the peaks was obtained. For clopyralid (Figure 4c.), SPIDER achieved a better simulation and was able to simulate most of the observed peaks, while MACRO only simulated one peak (in March 2010) at a concentration larger than the LOQ.

Brown et al. (2002) proposed a semi-quantitative approach to evaluating a catchment model intended for pesticide management purposes, whereby simulated loads and maximum annual concentrations were evaluated as being within a factor of 2, 5 or 10 of measured values. Applying this approach to the data in Table A–6, both models gave good simulations of maximum concentrations of chlorotoluron and mecoprop (many simulations within a factor of 2 of observed values, all simulations within a factor of 5). Simulations of loads for these two compounds were also good with the exception of 2009/10 where MACRO in particular over-estimated the loads significantly. All simulated maximum concentrations and loads of carbetamide were within a factor of 10 of measured values, whilst propyzamide was often well simulated (factors of 2-5) except in 2008/09 when transport was greatly under-estimated by both models. SPIDER gave much better simulations than MACRO for clopyralid, whereas both models failed to match the observed behaviour for MCPA as noted above.

3.3 Uncertainty analysis for SPIDER and MACRO simulations

3.3.1 Uncertainty in the rainfall data

The observed flow for each hydrological year and for the simulation period 2007-2011 was bounded for some periods by the simulations from the two rainfall datasets (measured +/-10%) for both models (Figure A–6). However, the effect of uncertainty in the rainfall was more evident for MACRO. The exceptions were for hydrological years 2008/09 and 2010/11 when both models and only SPIDER, respectively, under-estimated the flow even after increasing the rainfall by 10%. Uncertainty in the rainfall data had a big impact on the simulation of stream flow for the two models in both high- and low-flow periods but the greatest relative change during storm flow events was observed when increasing the rainfall by 10%. A large effect on the simulated flow was observed for the end of low-flow periods using MACRO; a great improvement was observed by increasing the rainfall data by 10% since the model predicted some of the peaks that were not simulated previously. A similar behaviour was observed from SPIDER but the impact was smaller than for MACRO during low-flow periods. In addition, the difference between the simulated and observed flow in the timing of flow recovery after summer for both rainfall datasets was approximately 15 days for SPIDER, but almost one month for MACRO.

3.3.2 Uncertainty in the application date

Table 2 and Table A–7 show the variation in simulated pesticide loads over a 4-year period (kg/4 years) on dates when pesticide application is likely to occur for carbetamide and the other pesticides, respectively. The simulated loads from both models over a 4-year period for carbetamide were within a factor of two for most of the application dates in November compared to the observed load and were very similar between models. Application dates in mid- or late November showed better agreement with the measured load.

Uncertainty in the application date had a smaller impact on pesticide loads for some pesticides. For instance, the resulting loads for propyzamide using SPIDER and for clopyralid using MACRO varied by less than 0.3 kg across all application dates simulated. Mecroprop was the pesticide that showed the greatest variation in loads (more than 100 kg using both models); this compound is impersistent in soil so timing of application relative to timing of storm event is an important influence on simulations. Across the full dataset, there was a tendency for SPIDER to be more sensitive than MACRO to changes in application date.

3.3.3 Uncertainty in pesticide sorption and degradation

The effect of uncertainty from using average sorption and degradation data was analysed by comparing pesticide loads for simulations using combinations of extreme input data (maximum and minimum sorption and degradation values derived from the literature). The results of this bounds analysis are shown in Table 3 and Table A–8 for carbetamide and the other pesticides, respectively. This source of uncertainty had a greater impact on the simulated pesticide load than the uncertainty due to the application date, but the impact was again compound-specific.

Simulated loads were greatest for the combination of minimum K_{oc} and maximum half-life while the smallest loads were obtained by using maximum K_{oc} and minimum half-life. Extreme differences in simulated loads were obtained for MCPA; losses were negligible when using the minimum half-life value because the pesticide largely degraded in soil before the first flow event after application. Uncertainty in pesticide sorption had a bigger impact on the simulation of loads than uncertainty in degradation. The simulated ranges for both models covered the observed loads for most pesticide-model combinations. For example, the range of simulated loads from both models covered the observed load of 23.3 kg over 4 years at the catchment outlet for carbetamide (Table 3); this measured load corresponds to 0.36 g ha^{-1} yr^{-1} or 0.023% of applied carbetamide.

4 Discussion

4.1 Simulation of water flow

The hydrograph simulations from MACRO and SPIDER showed a reasonably good match in the timing and size of peak flow compared to the measured data. However, there was a trend for the models to over-estimate flow during periods of greatest flow; this may be attributable to structural errors within the models due to their simplified representation of the environment, but might also relate to flood control measures within the catchment that were not included in the model. Flood management in the Wensum includes changes in the course and dimensions of the river channel, changes in the connectivity between the river and the floodplain, removal of the bed substrate and deposited fine sediment, control of aquatic and riparian vegetation and alterations to the water levels within the channel and downstream movement of sediment (mill weirs, sluices) (Sear et al., 2006). Model efficiency values after calibration showed that the simulation of the water flow from MACRO (NSE = 0.56) was better than that achieved by SPIDER (NSE = 0.34). Renaud and Brown (2008) obtained very similar model performance for SPIDER in two field studies in the UK (at Cockle Park, Northumberland and Maidwell, Northamptonshire) but in both cases SPIDER simulations were not calibrated. The authors found similar model performance for MACRO (NSE = 0.35) and SPIDER

(NSE = 0.32) for the site located at Cockle Park, whilst for the site located at Maidwell, model performance without calibration was considerably better for SPIDER (NSE = 0.23) than for MACRO (NSE = -0.61). The water flow simulation from SPIDER was significantly improved for Maidwell after minimal calibration (NSE = 0.55). Calibration to improve simulation of drainage early in the period was achieved through small changes to the water content at field capacity and the initial water content of the soil, a reduction in the rate of recharge and an increase in the fraction of soil in contact with macropores. Both studies reported by Renaud and Brown (2008) were carried out at field scale where input parameters are likely to have smaller variability than that observed at catchment level so that less uncertainty was expected in model results.

The GW model significantly improved model efficiency for both models before model calibration (from NSE = -0.12 to NSE = 0.45 for MACRO and from NSE = -0.19 to NSE = 0.23 for SPIDER). Tediosi et al. (2013) also reported a coupled model using MACRO and a simple groundwater model to simulate the water flow in a small (15.5 ha) headwater sub-catchment located in the Upper Cherwell in central England. This groundwater model was developed based on a variation of the saturated thickness (Rushton and Youngs, 2010) using typical values of hydraulic conductivity and specific yield for the study area. According to the authors, this approach showed a good representation of the recession periods in the hydrographs and the simulation of the water flow which increased model efficiency from 0.02 to 0.56 and the hydrograph was only affected by under-estimation of flow during periods of either standing snow or low precipitation.

Model calibration was applied to the simulations using MACRO and SPIDER to increase water flow and to improve the simulation of the low-flow periods. The simulation of recovery flow was slightly improved in both models; however, no improvements were observed for the recession periods of flow in the summer (Figure A–3). SPIDER generally simulated peaks in drainflow earlier than MACRO at the end of the lowest flow periods. One possible reason is an over-estimation of evapotranspiration by MACRO. Besien et al. (1997) suggested that such an over-estimation caused the model to miss drainflow events generated by low rainfall in early spring affecting both drainflow and pesticide simulations for that period. In this study, it was found that over-estimation of evapotranspiration was also critical for the early autumn period (i.e. at the beginning of the winter flow period), which caused the model to misrepresent the flow recovery rate. Over-estimation of evapotranspiration by MACRO during the summer periods delays flow recovery, consequently causing the water flow simulation to miss drainflow and pesticide losses at those times. When pre-calculated evapotranspiration from SPIDER was used in MACRO, both drainflow and river flow showed an improvement in simulation of earlier drainflow events and in the flow rate at the end of the lowest flow periods (Figure A–7). This suggests that the FAO Penman–Monteith equation (Allen, 1998) used by SPIDER may be a better approach than the original Penman–Monteith equation (Monteith, 1965) used by MACRO for the calculation of the evapotranspiration under the study conditions. The FAO Penman–Monteith equation is recommended by Allen (1998) as it provides more consistent evapotranspiration values in all regions and climates.

A common challenge in hydrological modelling is to obtain accurate rainfall data since it is the main driver controlling the accuracy of hydrological and solute simulations (Bardossy and Das, 2008). Rainfall gauge measurements are subject to uncertainty, and under-estimation of rainfall from rain gauge measurements is common during low intensity precipitation and/or high winds (Ciach, 2003; Wang et al., 2008). As errors in rainfall measurements are variable over time, the impact on water flow simulation varies during the hydrological year. Owing to the complex nature of rainfall, model calibration from this source of uncertainty can only be achieved by the use of more accurate measurements. Other hydrological models such as rainfall-runoff models used for flood forecasting have also been affected by rainfall uncertainty (Bardossy and Das, 2008; Moulin et al., 2009). Moulin et al. (2009) suggested that meteorological services should deliver rainfall data along with information about the confidence intervals generated in real time. This information would be useful in applying probabilistic approaches that could express uncertainty in hydrological simulations. In addition, climate data and particularly the precipitation falling over a location vary both spatially and temporally (Obled et al., 1994; Wood et al., 1988). A limited number of rain gauges may not be able to capture the spatial variability of rainfall, particularly on large catchments, adding errors to model results.

4.2 Pesticide simulation

This is the first time that SPIDER has been tested using long-term monitoring data collected for a relatively large catchment. Both models were able to simulate a large number of the observed peaks for pesticides at the catchment outlet as well as the overall pattern of behaviour of most of the pesticides despite the simple nature of the models and not including surface runoff in the simulations. Apart from the peaks that MACRO missed in early autumn due to under-estimation in the flow, most of the simulations showed reasonable agreement with measured behaviour; however, some disagreements were observed in the timing and magnitude of peaks. The exception was for clopyralid and MCPA where significant differences in the simulations were observed both relative to measured data and between models.

Holvoet et al. (2007) considered that in-stream processes and state variables (e.g. microbial activity, dissolved oxygen concentration, pH, sedimentation, re-suspension) have a significant impact on modelling pesticides at the catchment-scale. However, in the present study, the modelling framework was able to satisfactorily simulate water flow from a relatively large catchment like the Wensum and predict reasonably well the pattern of pesticide concentrations even though the framework ignored in-stream processes suggesting that the river system had a relatively minor influence on patterns of pesticide concentrations at the catchment outlet. Modelling results suggested that pesticide concentrations in water were driven primarily by field-scale processes. There was no major difference between simulations from a modelling framework composed of field-scale models and from a catchment-scale model when applied to a medium-sized catchment in Eastern England. An implication is that provided field-scale processes are well captured by a model, then it should be possible to approximate pesticide export at the catchment scale. This is in agreement with other studies that have suggested the possibility to predict the order of magnitude of pesticide losses from catchments based on information on pesticide and soil properties plus pesticide usage (Pistocchi, 2013).

The best simulations were observed for pesticides that are normally applied in late autumn such as chlorotoluron, mecoprop, carbetamide and propyzamide. These pesticides are mainly applied to a single crop type, so uncertainty in their usage patterns (i.e. application date and amount) is relatively small. For instance, chlorotoluron is exclusively applied as a pre- or early post-emergence herbicide to winter cereals to control annual grasses and broad leaved weeds. In addition, the relatively large degradation half-life (59 days) means that differences in the application date will have relatively little impact on the timing and magnitude of pesticide peaks simulated by the models.

Propyzamide and carbetamide showed a good agreement between the pattern of the simulated concentrations and the measured data but with some disagreements in the magnitude of the peaks. These pesticides are mainly used to control broadleaved weeds and blackgrass that is resistant to other herbicides. Pesticide application takes place between October and the end of February depending on soil moisture and temperature. The relatively wide window of time for application and the specific environmental conditions required mean that the use of a uniform and fixed application date would generate uncertainty that will mainly affect the magnitude of the peaks. This uncertainty in the application date had a greater impact on the simulation of carbetamide than propyzamide losses. The moderately large K_{oc} (292 ml g^{-1}) and half-life (47 days) selected to simulate propyzamide mean that the pesticide binds strongly to soils and persists for a long time. In contrast, carbetamide has both weaker soil sorption (K_{oc} = 89 ml g^{-1}) and shorter half-life (10.9 days) so if there is a delay between application date and a storm event, pesticide transfers to tile drains would be reduced due to pesticide degradation.

Clopyralid and MCPA concentrations proved difficult to simulate due to the complex and uncertain usage pattern of these pesticides. Clopyralid is applied to a wide range of crops including cereals, grassland, amenity grass/lawns, OSR, brassicas and maize and MCPA is used on cereals, grassland and amenity grass/lawns. These post-emergence herbicides are mainly applied during spring and throughout the summer when weeds are actively growing. Since these herbicides can be applied during a very wide window of time, the uncertainty generated by the use of fixed application dates can greatly affect the simulation. Different authors have suggested supplying application date as a probability distribution in fate models (Holvoet et al., 2005; Lindahl et al., 2005). However, this approach also requires knowledge of the distribution of application dates throughout the catchment. Gericke et al. (2010) used phenological data for different crops along with climate data to estimate application dates in Germany and the Czech Republic; satisfactory results were obtained when comparing estimated to actual application dates. This approach can provide a broader amount of information to estimate application dates but the methodology requires further development and validation under different environmental conditions.

For clopyralid, MACRO only predicted three small peaks that were due to pesticide drainflow, whilst the model missed other events that SPIDER simulated. It was observed that important losses of clopyralid could be due to sub-lateral flow (through-flow); SPIDER simulates this whereas MACRO does not account for pesticide loss by this route. Clopyralid was different from other compounds where drainflow dominated because losses occurred in late spring when drains may not be flowing and sub-lateral flow may be a relatively important contributor to catchment hydrology.

The uncertainty analyses for the simulation pesticide losses in the present study showed that uncertainty from individual input parameters could explain some of the observed disagreements in the simulation from the two models. Simulated loads from both uncertainty analyses (application date and sorption and degradation data) using both models generally covered the observed load for the simulation period. However, a combination of different sources of uncertainties might be the best explanation of discrepancies in simulated concentrations. The exception was for MCPA due to the lack of simulated drainflow on days when emissions were observed and for clopyralid using MACRO for the reasons explained above.

The impact on the simulated loads of uncertainty in both application timing and pesticide properties was model- and compound-specific. Boithias et al. (2014) carried out a sensitivity study using plausible ranges of application dates for two contrasting pre-emergence herbicides in SWAT. The authors also found that the effect of the application date was a pesticide-specific factor influenced by their bioavailability and hence by sorption and degradation. For runoff models like SWAT pesticide sorption was shown to be more important than degradation in determining the availability of pesticides in the runoff interaction zone. For preferential flow models, the availability for pesticide loss would depend on the leaching potential of pesticides to reach tile drains where both parameters (degradation and sorption) are known to be important (Arias-Estevez et al., 2008; Carter, 2000). Pesticides with high leaching potential likely to reach tile drains via preferential flow are characterised by having slower degradation rates and weaker soil sorption (Gardner, 2014).

Model evaluation was in some cases affected by the resolution of the measured pesticide concentrations. Some important emissions predicted by the models could not be evaluated due to the absence of monitoring data for those days. Monitoring frequency varies within crop years and a large proportion of none detections was observed for most herbicides. For instance, only 73 of the 395 samples taken between September 2007 and November 2011 for the analysis of chlorotoluron contained residues above the LoQ; however, during this period SPIDER predicted 139 days with emissions on days when samples were not taken. The CSF monitoring programme has a moderate sampling frequency (an average of one sample every four days) and this resolution is useful to analyse pesticide trends and to undertake model evaluation; however, modelling results show that the monitoring programme could be made more efficient by applying a more variable sampling frequency during the year. A report from the CSF (2012) explains that the monitoring design was based on the major crop types present in the catchment and highlights that a large proportion of the pesticides analysed are not detected in the samples. This report notes that predicting the likelihood of occurrence of a pesticide is a complex task that is influenced by many factors such as pesticide properties, soil types, and pesticide usage and drainage systems (CSF, 2012). Pesticide fate modelling takes into account all these factors and helps avoid bias and speculative methodologies. Fate models have been shown to be a useful tool to improve the design of monitoring programmes (e.g. by focusing sampling collection on days when pesticides are most likely to be present) and can be easily incorporated into programmes without a big financial investment.

5 Conclusions

The modelling framework simulated fairly well the main sources of water flow contributing to the river network in the Wensum catchment and their associated pesticide losses though there was variable performance between individual pesticides. As the framework excluded the simulation of in-stream processes, results suggest that field-scale processes may be important in determining patterns of pesticide contamination at the catchment outlet. The models showed a better performance for pesticide losses coming from pre- or early post-emergence herbicides normally applied during autumn probably because of their less complex usage patterns; an alternative explanation is that important hydrological pathways resulting in pesticide losses during spring and summer periods were poorly simulation by the models. Uncertainty analyses of sensitive input parameters showed that the impact of parameter variation on pesticide simulations was compound-specific. The simulation of low-flow periods was greatly affected by uncertainty from rain gauge measurements and the simulation of evapotranspiration. More studies into the combined effect of uncertainties in fate modelling as well as in pesticide-specific uncertainty would strengthen the understanding of their impact on simulations.

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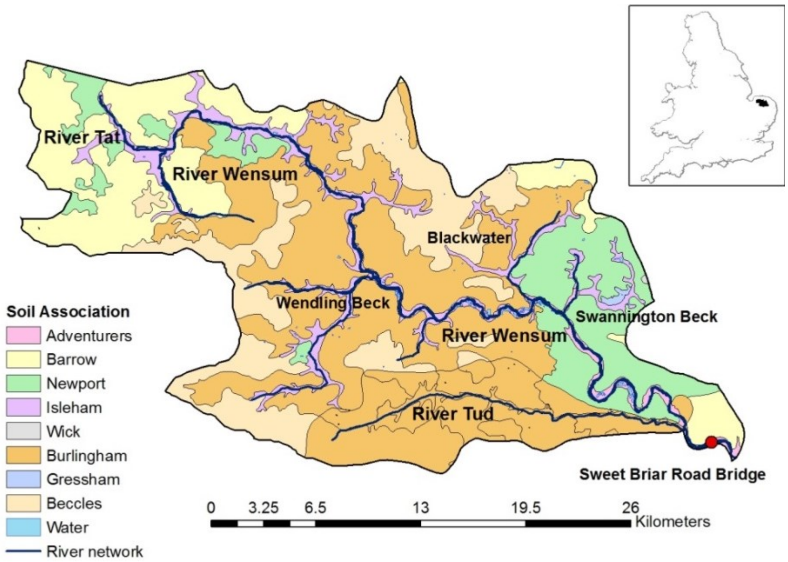


Figure 1 Wensum catchment showing the river network and the catchment outlet at Sweet Briar Road Bridge. Inset: location of the Wensum catchment within England and Wales.

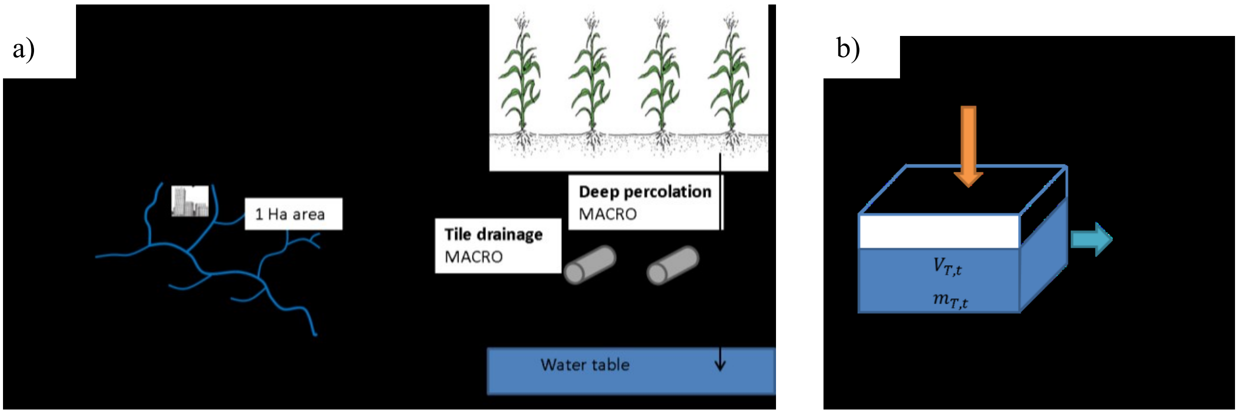


Figure 2 Conceptual model of a) the framework using MACRO and b) the groundwater mixing model.

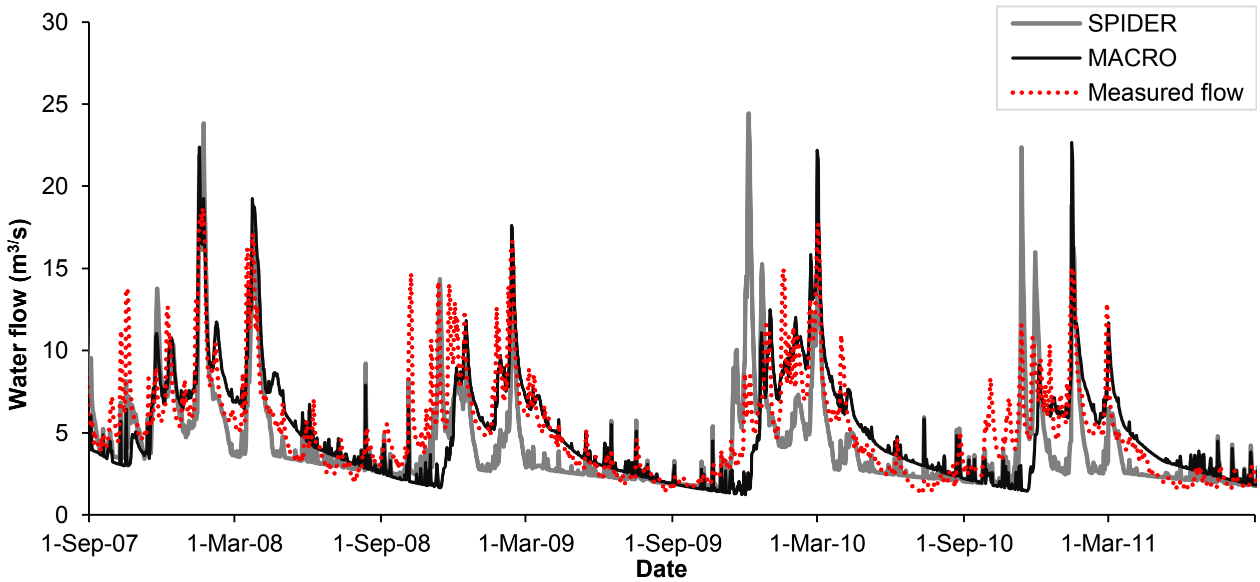


Figure 3 Comparison of the measured and simulated water flow (calibrated simulations) by MACRO and SPIDER. Measured flow supplied by the Environment Agency.

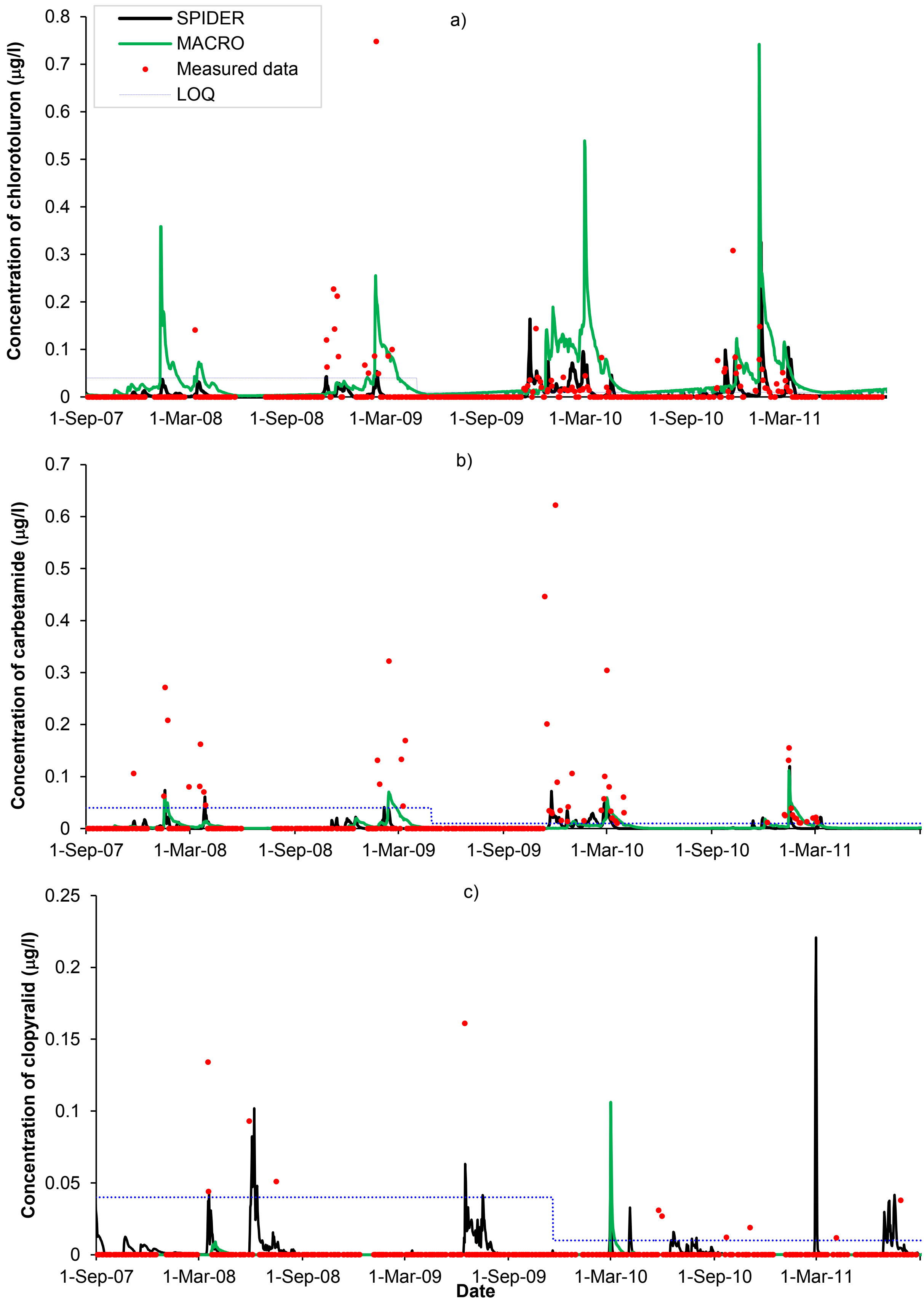


Figure 4 Comparison of measured pesticide concentrations with those simulated by SPIDER and MACRO for a) chlorotoluron, b) carbetamide and c) clopyralid. The dotted line indicates the LoQ. Pesticide concentrations <LOQ represented with a value of zero. Measured pesticide data supplied by the Environment Agency.

Table 1 Comparison between observed and simulated flow for each hydrological year from the model framework using MACRO and SPIDER before and after calibration including their NSE values and the measured rainfall.

Hydrological year	Rainfall (mm)	Uncalibrated				Calibrated			
		Simulated flow (% of the observed flow)		NS		Simulated flow (% of the observed flow)		NS	
		MACRO	SPIDER	MACRO	SPIDER	MACRO	SPIDER	MACRO	SPIDER
2007/08	671.2	96.3	74.8	0.61	0.35	98.6	89.6	0.63	0.59
2008/09	543.3	73.5	50.2	0.10	-0.22	81.0	69.0	0.33	0.22
2009/10	593.0	91.2	77.3	0.64	0.33	100.7	91.9	0.72	0.15
2010/11	586.3	80.5	65.7	0.19	0.15	91.1	80.8	0.39	0.22
Total 4 years	2,393.8	85.9	67.2	0.45	0.23	93.0	83.0	0.56	0.34

Table 2 Loads of carbetamide simulated by SPIDER and MACRO for different application dates in November and comparison with the observed value.

	1 Nov	5 Nov	10 Nov	15 Nov	20 Nov	25 Nov	30 Nov	Observed data
	Loads (kg/4 years)							
SPIDER	6.05	9.99	14.1	19.3	17.3	21.7	22.7	23.3
MACRO	11.5	14.5	21.5	22.5	15.3	14.2	20.1	

Table 3 Loads of carbetamide simulated by SPIDER and MACRO using combinations of maximum and minimum sorption and degradation values, together with the simulated load using average inputs and the observed value.

	Avg. K_{oc} Avg. DT_{50}	Max. K_{oc} Max DT_{50}	Max. K_{oc} Min. DT_{50}	Min. K_{oc} Max DT_{50}	Min. K_{oc} Min. DT_{50}	Measured data
	Loads (kg/4 years)					
SPIDER	6.05	11.3	0.14	43.1	0.48	23.3
MACRO	11.5	28.6	1.56	74.1	1.83	

Supplementary information

Methodology

Table A–1 Pesticide properties used in the models and sorption and degradation ranges used for the uncertainty analysis.

Pesticide	Koc (mL g^{-1})[a]	DT_{50} soil[a] (days)	Koc range[a] (mL g^{-1})	DT_{50} soil range[a] (days)	TREF (°C)	TRESP (K^{-1})	EXPB	Freundlich coefficient[b]
Carbetamide	89	10.9	59 - 118	4 - 29	20	0.08	0.7	0.93
Chlorotoluron	184	59	108 - 384	52 66	20	0.08	0.7	0.90
Clopyralid	4.9	11[d]	3.43 - 7.34	2 – 24[d]	10	0.001	0.01	0.76
MCPA	74	24	38 - 157	7 - 41	20	0.08	0.7	0.68
Mecoprop	20	8.2	-	-	20	0.08	0.7	0.90
Propyzamide	292[c]	47	-	-	20	0.08	0.7	0.90[c]

TREF: Reference temperature. TRESP: Exponent in the temperature response function. EXPB: Exponent in the degradation water response function. [a]Lewis et al. (2015), [b]Netherton and Brown (2010), [c]Pedersen et al. (1995). [d]Field-based degradation rate.

Table A–2 Crop areas in the Eastern region for target crops and arable land between 2005 and 2013.

	Crop area (ha)			
	2006[a]	**2008[b]**	**2010[c]**	**2012[d]**
Cereals	471,706	534,735	502,081	513,356
OSR	103,488	130,181	140,960	168,241
Beet	72,656	80,732	75,918	82,346
Total arable land	1,017,084*	987,447	967,621	990,137
	2005[e]	**2009[f]**	**2013[g]**	
Grassland	29,137	36,103	37,065	

OSR: Oilseed rape. * Including set-aside
[a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013); [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010); [g]Garthwaite et al. (2014)

Table A–3 Pesticide usage information for the Eastern region of the UK.

Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)	Pesticide / Crop / Year	Total area treated with pesticide (ha)	Total pesticide weight applied (kg)
Chlorotoluron	**Cereals**		**Carbetamide**	**OSR**	
2006[a]	19,548	32,607	2006[a]	12,121	25,086
2008[b]	44,697	96,841	2008[b]	30,383	61,725
2010[c]	101,014	178,711	2010[c]	26,066	49,453
2012[d]	58,293	84,938	2012[d]	27,229	45,596
Clopyralid	**Cereals**		**Clopyralid**	**Beet**	
2006[a]	811	151	2006[a]	65,273	4,810

2008[b]	1,964	175	2008[b]	64,532	4,856
2010[c]	7,797	255	2010[c]	107,283	7,835
2012[d]	12,152	830	2012[d]	58,830	4,673
Clopyralid	**Grassland**		**MCPA**	**Grassland**	
2005[e]	9,233	1,311	2005[e]	103,504	131,101
2009[f]	23,988	4,597	2009[f]	20,997	20,469
Clopyralid	**ORS**		**MCPA**	**Cereals**	
2006[a]	34,848	2,767	2006[a]	19,977	14,910
2008[b]	94,076	7,729	2008[b]	9,826	5,867
2010[c]	98,711	7,794	2010[c]	21,980	13,016
2012[d]	137,486	11,781	2012[d]	17,575	16,128
Mecoprop	**Cereals**		**Propyzamide**	**OSR**	
2006[a]	167,289	98,793	2006[a]	81,144	60,493
2008[b]	187,286	102,590	2008[b]	110,357	83,970
2010[c]	180,532	95,611	2010[c]	161,367	125,987
2012[d]	135,446	77,745	2012[d]	215,375	171,889

[a]Garthwaite et al. (2007); [b]Garthwaite et al. (2009); [c]Garthwaite et al. (2011); [d]Garthwaite et al. (2013); [e]Garthwaite et al. (2006); [f]Garthwaite et al. (2010)

Table A–4 Limits of quantification for the pesticides data supplied by the Environment Agency

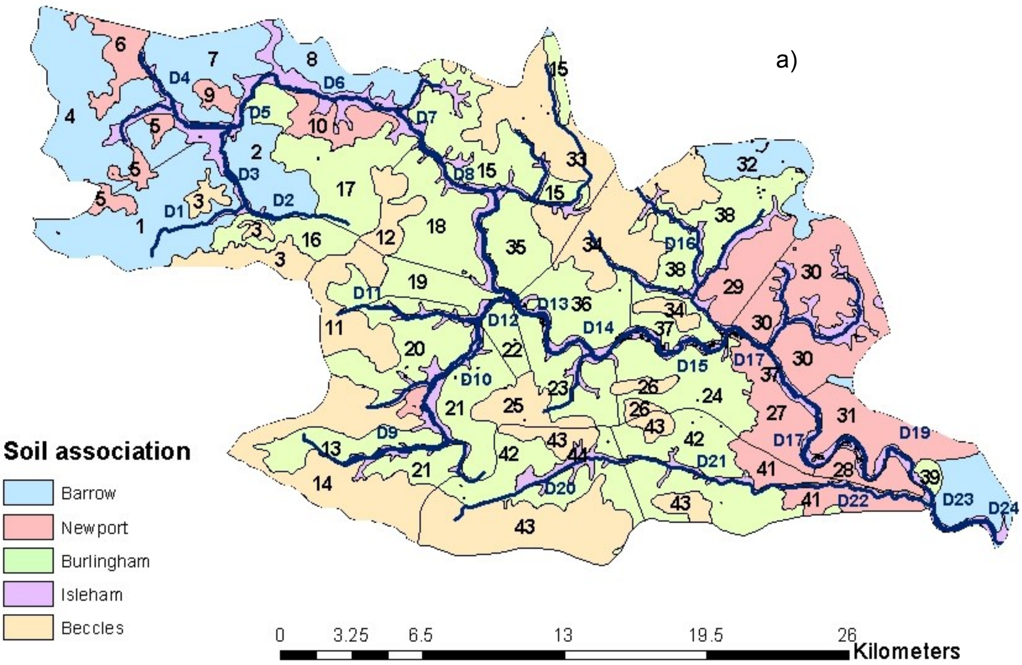
Pesticide	LOQ (µg/l) September 2006 to April 2009/*April 2010	LOQ (µg/l) May 2009/*May2010 to December 2011
Carbetamide	0.04	0.01
Chlorotoluron	0.04	0.01
Clopyralid	0.04*	0.01*
MCPA	0.04*	0.005*
Mecoprop	0.04*	0.005*
Propyzamide	0.005	0.005

Table A–5 Pesticide degradation values in water and sediment obtained from laboratory studies and Freundlich coefficients used in SPIDER

Pesticide	**DT_{50} water (days)[a]**	**DT_{50} sediment (days)[a]**	**Freundlich coefficient[a]**
Carbetamide	9.1	55.5	0.93
Chlorotoluron	42	352	0.90
Clopyralid	148	1000[b]	0.85*
MCPA	13.5	17	0.85*
Mecoprop	37	50	0.90
Propyzamide	21	94	0.90

[a]Lewis et al. (2015), [b]Netherton and Brown (2010). *Values adjusted to avoid sorption conflicts in the model because the reported values were to small (0.76 and 0.68 for clopyralid and MCPA, respectively).

Figure A–1 Location of meteorological stations.



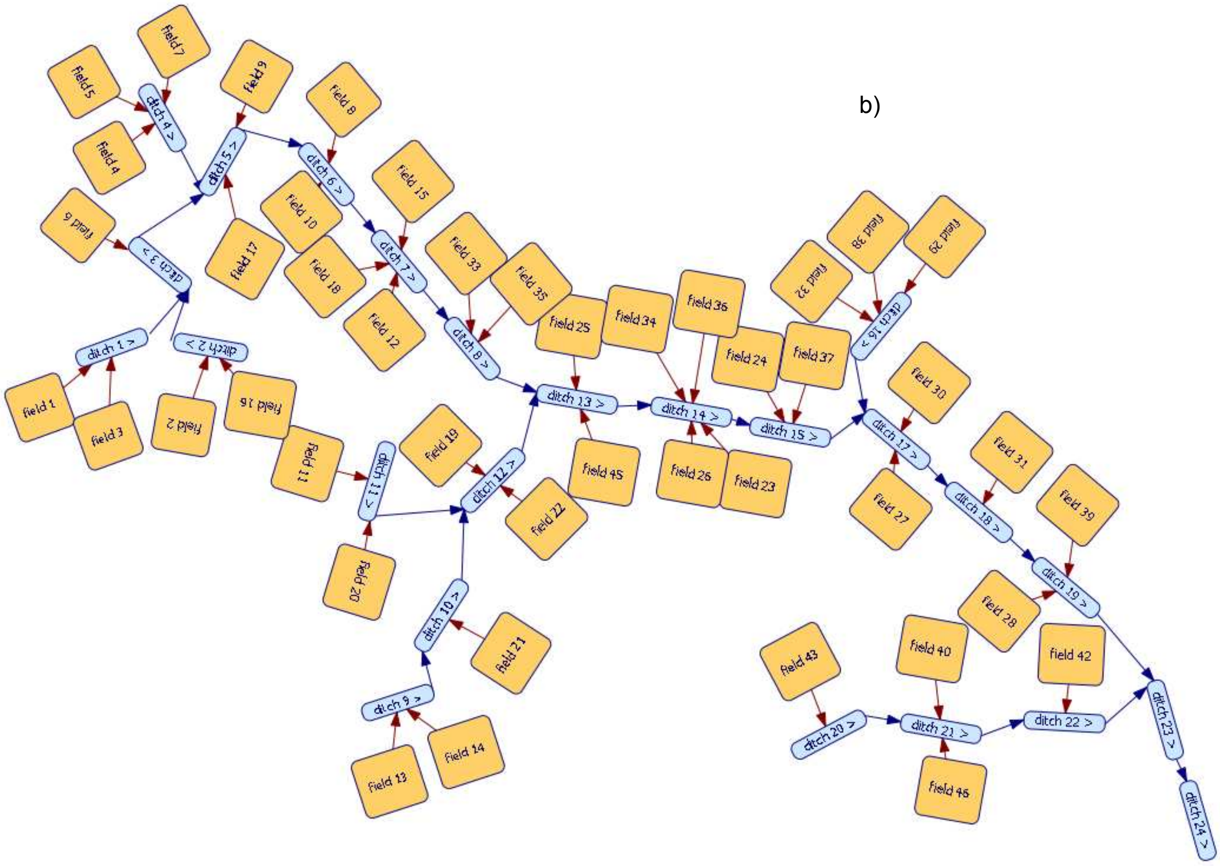
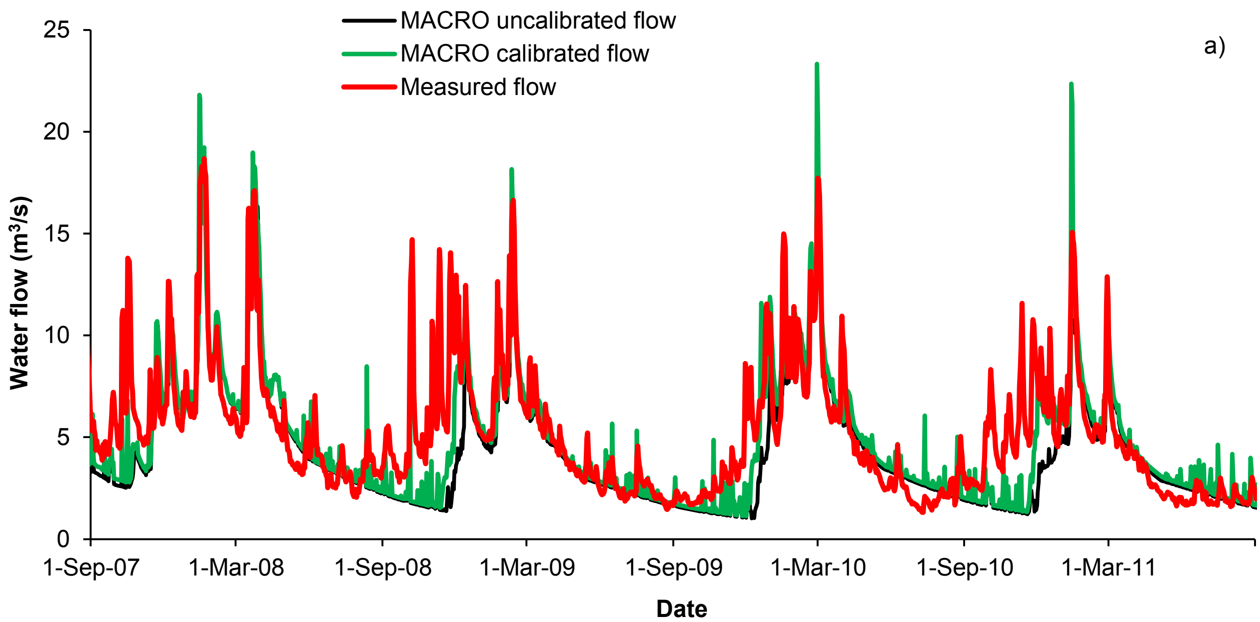
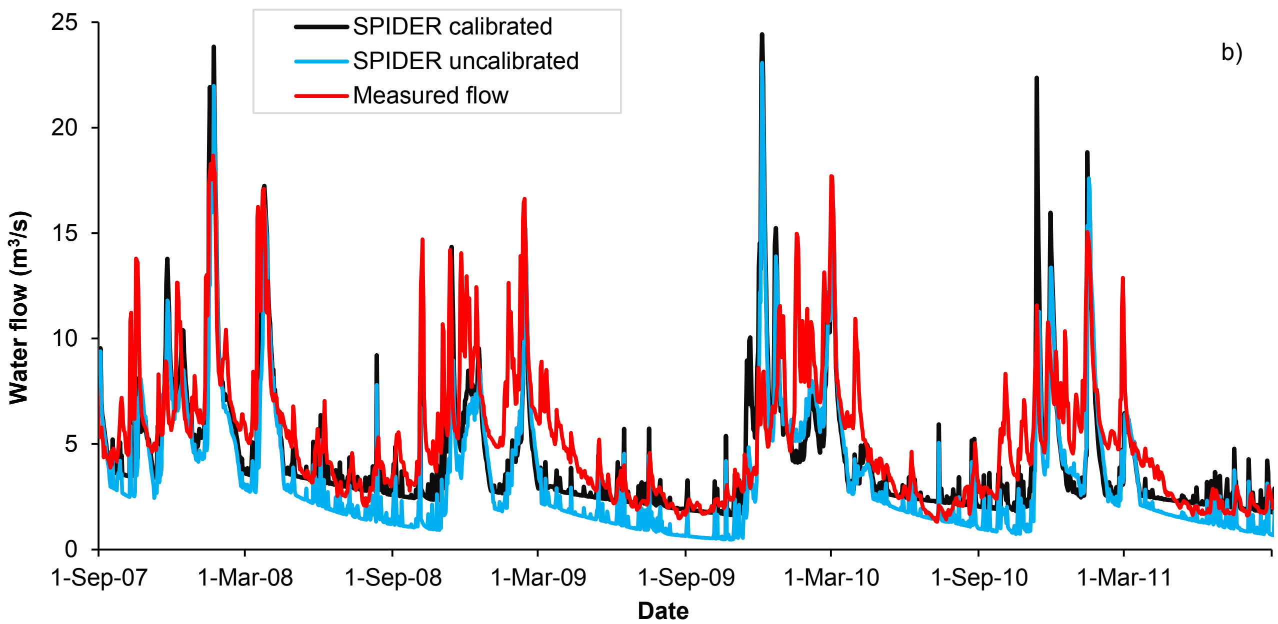


Figure A–2 a) Division of the Wensum catchment into 44 land blocks and 24 streams reaches. b) Conceptual scheme using SPIDER for the Wensum catchment.

Results

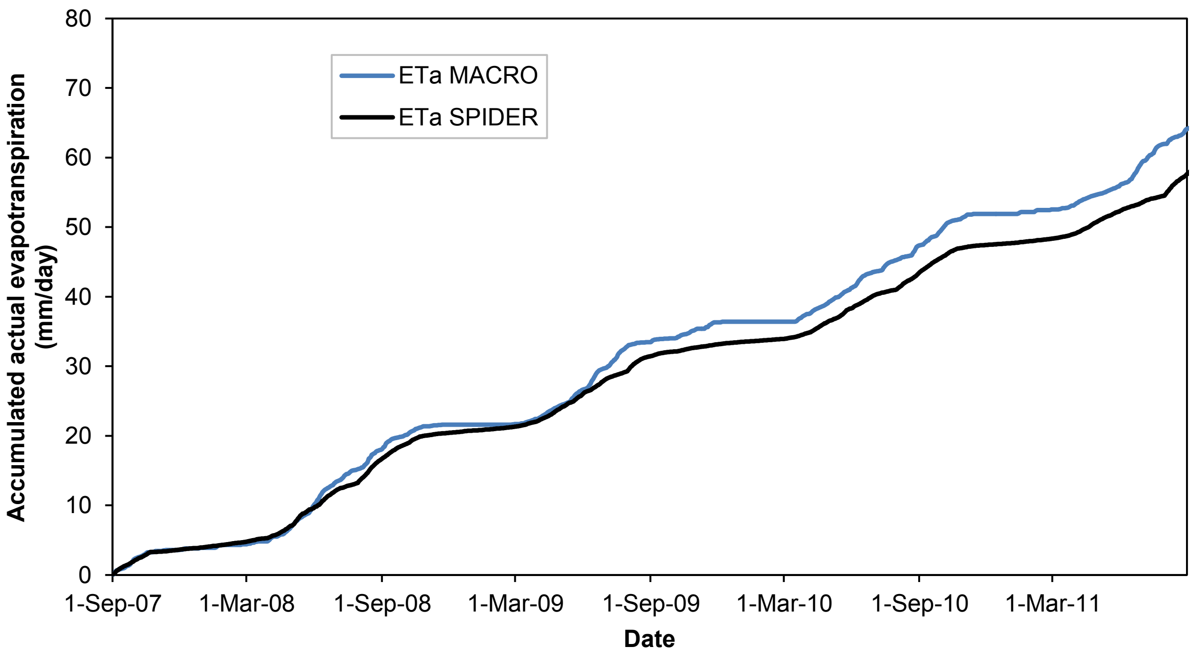




825

826 **Figure A–3** Comparison of the uncalibrated and calibrated simulation of the water flow using a) MACRO and
827 b) SPIDER with the measured flow in the Wensum catchment. Measured flow supplied by the Environment
828 Agency.

829



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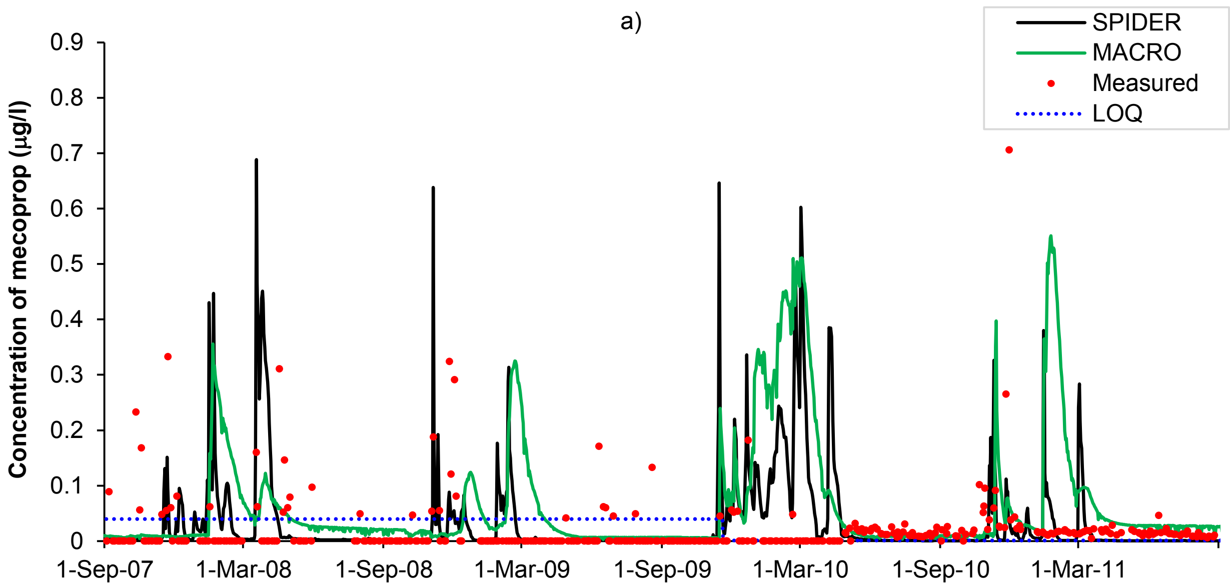
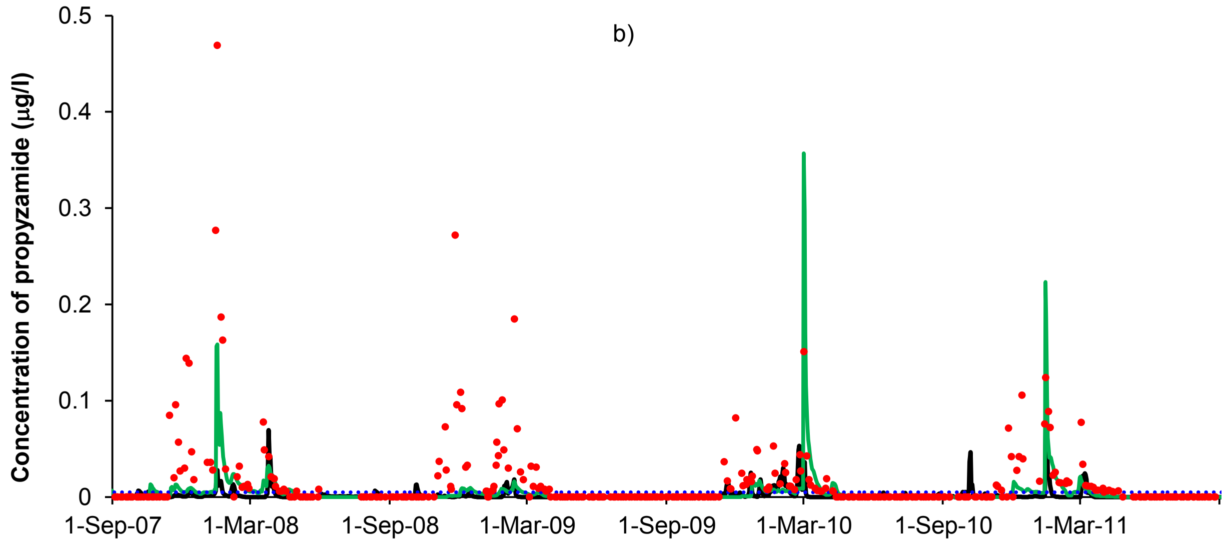
831 **Figure A–4** Comparison of the accumulated actual evapotranspiration simulated by MACRO and SPIDER.

832


a)
SPIDER
MACRO
Measured
LOQ
Concentration of mecoprop (µg/l)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1-Sep-07
1-Mar-08
1-Sep-08
1-Mar-09
1-Sep-09
1-Mar-10
1-Sep-10
1-Mar-11


b)
Concentration of propyzamide (µg/l)
0.5
0.4
0.3
0.2
0.1
0
1-Sep-07
1-Mar-08
1-Sep-08
1-Mar-09
1-Sep-09
1-Mar-10
1-Sep-10
1-Mar-11

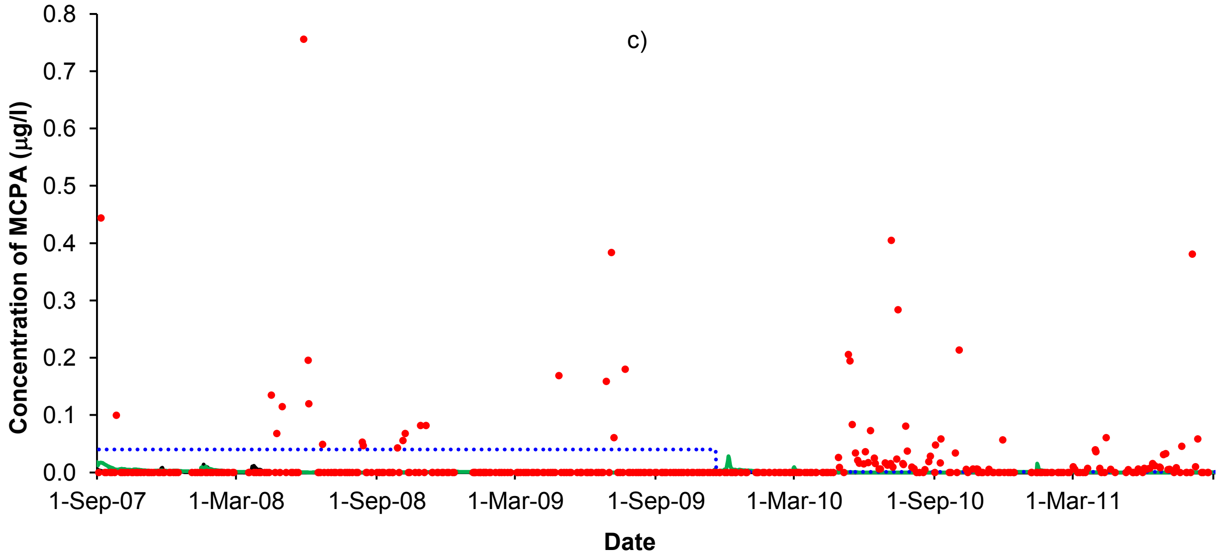
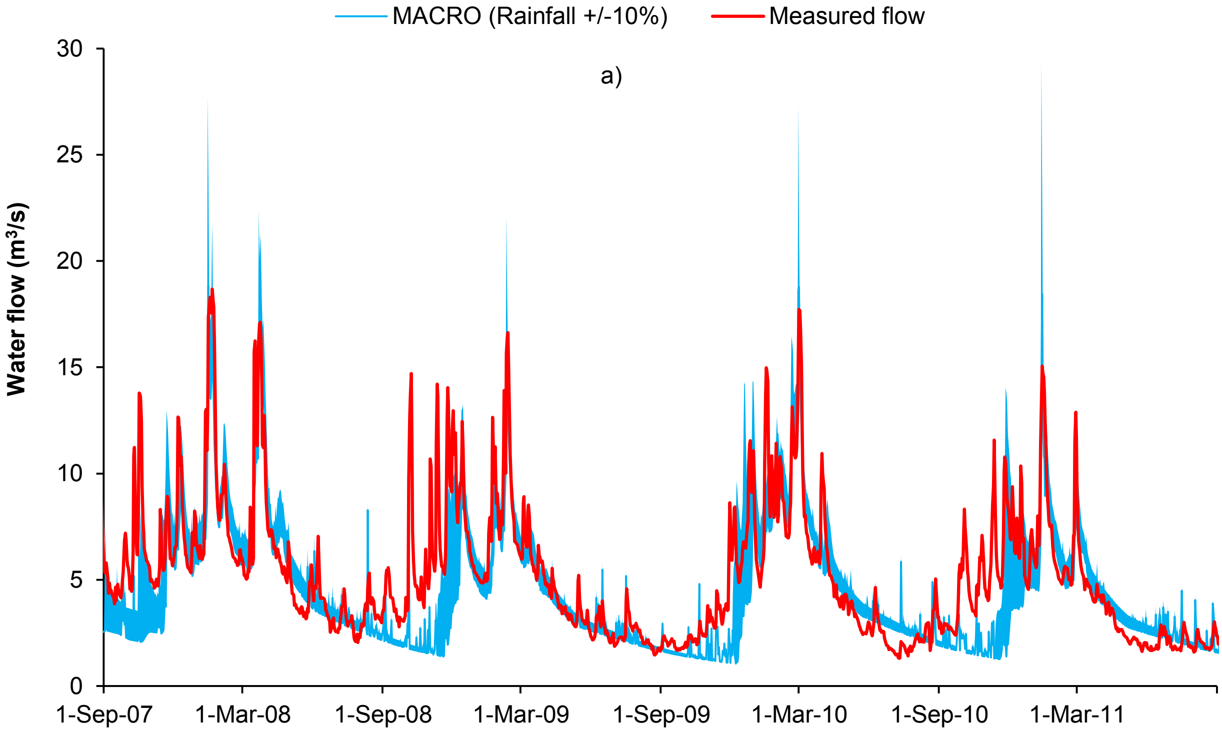

c)
Concentration of MCPA (µg/l)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1-Sep-07
1-Mar-08
1-Sep-08
1-Mar-09
1-Sep-09
1-Mar-10
1-Sep-10
1-Mar-11
Date

Figure A–5 Comparison of measured pesticide concentrations with those simulated by SPIDER and MACRO for a) mecoprop, b) propyzamide and c) MCPA. Measured pesticide concentration supplied by the Environment Agency.



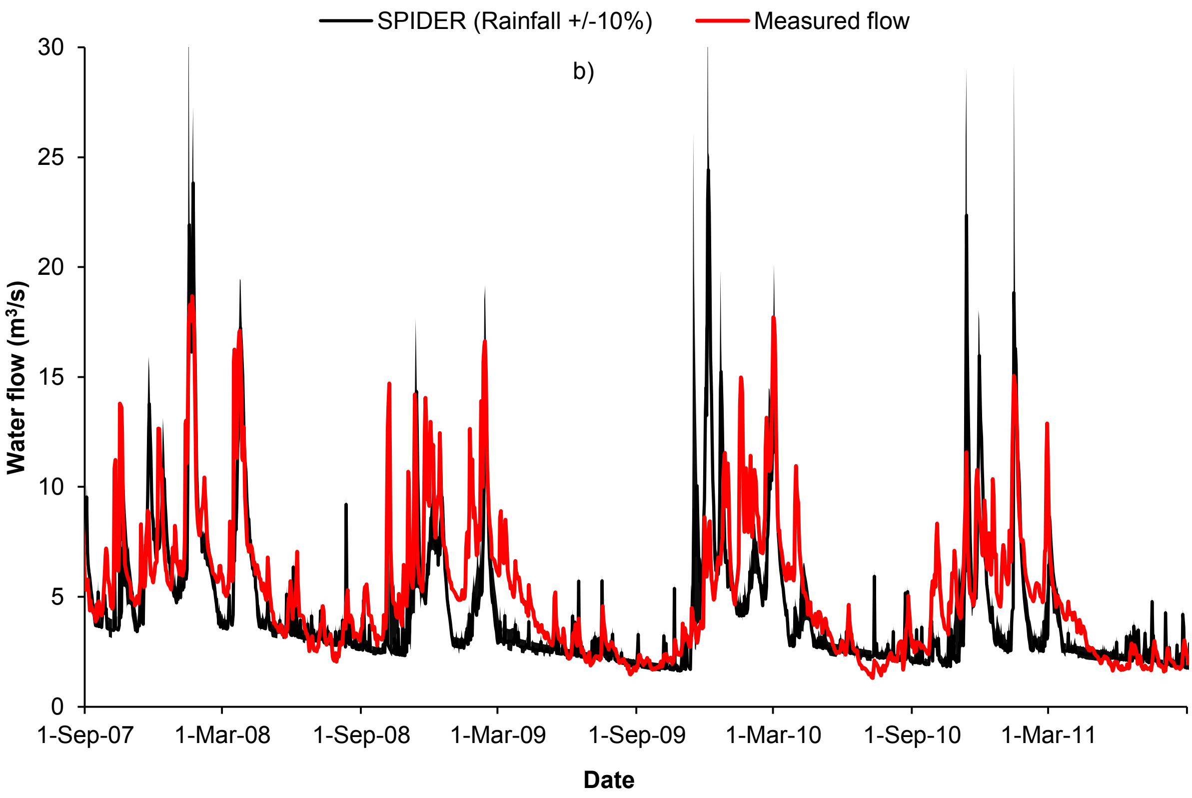


Figure A–6 Effect on the simulated water flow when decreasing and increasing the rainfall data by 10% using a) MACRO and b) SPIDER compared to the measured flow. Measured flow supplied by the Environment Agency.

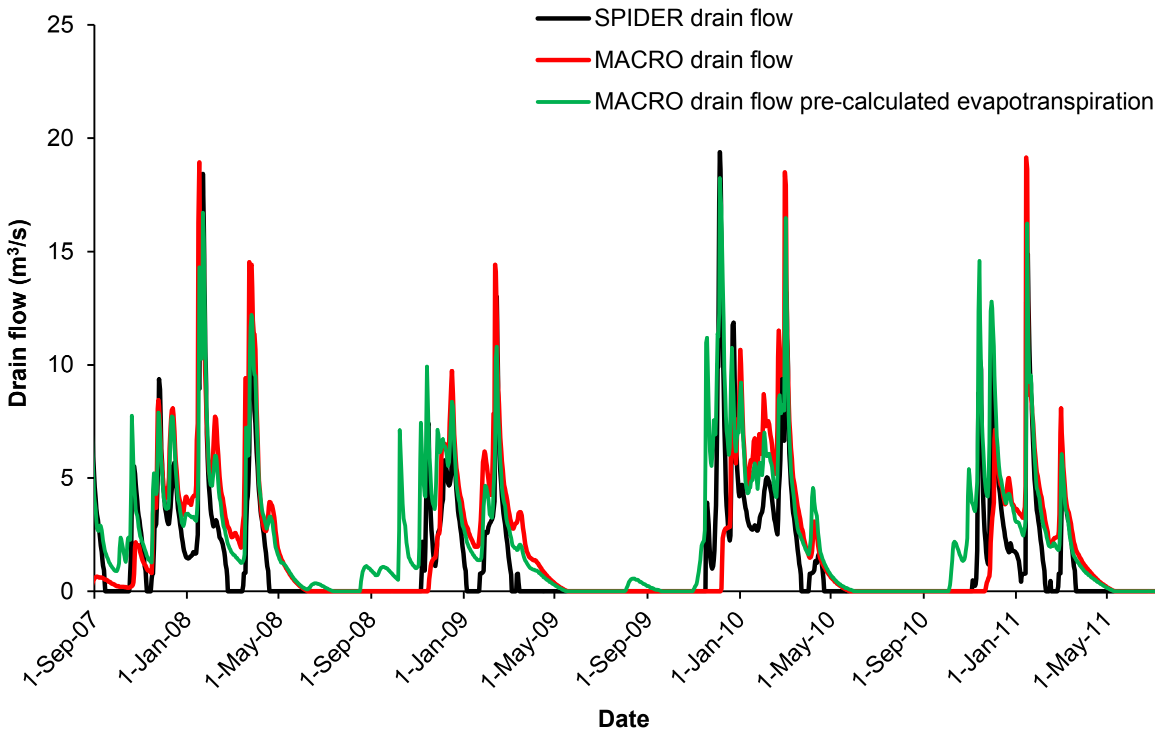


Figure A–7 Effect on the simulation of drain flow in MACRO from using the pre-calculated evapotranspiration from SPIDER and comparison with SPIDER and MACRO original simulation.

Table A–6 Loads and maximum concentrations of pesticides simulated by MACRO and SPIDER for different hydrological years and comparison with observed values.

	Observed	**SPIDER**	**MACRO**	**Observed**	**SPIDER**	**MACRO**
	Load (kg/year)			Max. Conc. (□g/l)		
Chlorotoluron						
2007/08	3.12	1.09	7.61	0.141	0.037	0.359
2008/09	8.83	0.933	5.48	0.227	0.053	0.256
2009/10	1.33	3.34	14.0	0.144	0.163	0.539
2010/11	3.06	3.32	10.1	0.308	0.326	0.742
Total 4 years	**16.3**	**8.68**	**37.1**			
Mecoprop						
2007/08	12.5	14.1	13.1	0.311	0.688	0.355
2008/09	9.70	3.86	8.94	0.324	0.638	0.325
2009/10	3.12	16.4	31.3	0.182	0.646	0.511
2010/11	5.37	4.26	15.2	0.706	0.380	0.551
Total 4 years	**30.7**	**38.6**	**68.6**			
Carbetamide						
2007/08	6.71	0.804	1.42	0.271	0.074	0.064
2008/09	3.95	0.488	1.56	0.322	0.041	0.071
2009/10	6.44	1.27	1.34	0.622	0.072	0.060
2010/11	1.85	0.557	1.45	0.155	0.120	0.112

Total 4 years	**19.0**	**3.12**	**5.77**			
Propyzamide						
2007/08	9.12	0.841	2.74	0.469	0.069	0.158
2008/09	5.88	0.272	0.463	0.272	0.018	0.016
2009/10	3.24	0.724	2.67	0.151	0.053	0.357
2010/11	3.21	0.737	1.758	0.124	0.108	0.223
Total 4 years	**21.4**	**2.57**	**7.63**			
Clopyralid						
2007/08	8.74	3.35	0.945	0.134	0.242	0.009
2008/09	6.81	2.57	0.011	0.161	0.325	0.000
2009/10	2.00	3.26	0.722	0.031	0.239	0.106
2010/11	1.42	3.17	0.086	0.038	0.456	0.000
Total 4 years	**19.0**	**12.3**	**1.76**			
MCPA						
2007/08	14.7	0.314	0.517	3.76	0.014	0.018
2008/09	7.48	0.007	0.038	0.384	0.001	0.002
2009/10	3.96	0.020	0.320	1.76	0.005	0.028
2010/11	2.11	0.005	0.108	3.76	5.32	0.015
Total 4 years	**28.3**	**0.346**	**0.983**			

Table A–7 Pesticide loads simulated by MACRO and SPIDER for different application dates and comparison with the observed value.

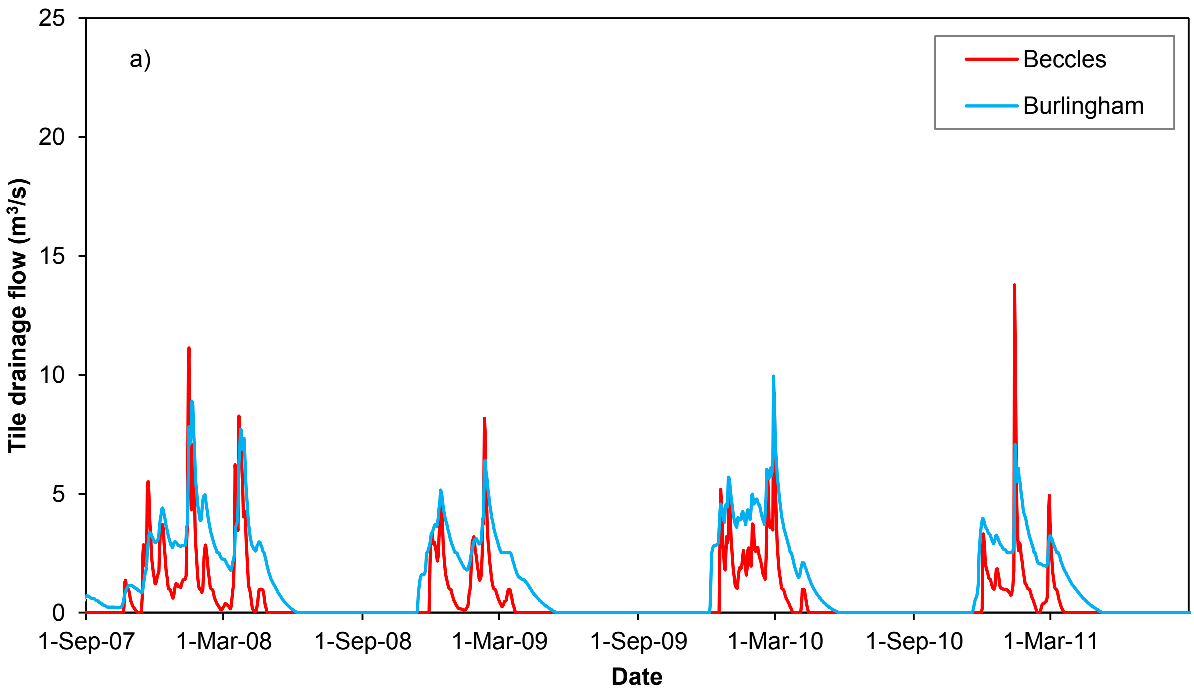
Pesticide/ Model	Loads (kg/4 years)							
	20 Oct	25 Oct*	30 Oct	4 Nov	9 Nov	14 Nov	19 Nov	Observed data
Chlorotoluron								
SPIDER	6.88	8.68	7.12	7.18	7.08	6.74	6.34	16.3
MACRO	31.5	37.1	45.5	45.8	52.9	43.7	39.5	
	25 Oct*	**30 Oct**	**4 Nov**	**9 Nov**	**14 Nov**	**19 Nov**	**24 Nov**	**Observed data**
Mecoprop								
SPIDER	38.6	60.2	90.3	139	186	198	188	30.7
MACRO	68.6	83.7	96.1	125	172	96.9	102	
	1 Nov	**5 Nov**	**10 Nov**	**15 Nov**	**20 Nov**	**25 Nov**	**30 Nov***	**Observed data**
Propyzamide								
SPIDER	2.60	2.67	2.69	2.57	2.61	2.43	2.57	21.4
MACRO	12.2	12.5	14.4	10.8	10.5	8.91	7.63	

	17 Mar 5 May	17 Mar 15 May	7 Mar 15 May	17 Mar 25 May	7 Mar 5 May	25 Feb 15 May	7 Mar 25 May	25 Feb* 25 May	25 Feb 5 May	Observed data
Clopyralid										
SPIDER	0.855	1.17	1.24	1.96	11.8	12.3	12.9	13.0	22.8	19.0
MACRO	0.186	0.186	0.230	0.186	0.230	0.670	0.230	0.669	0.669	

* Typical application date

Table A–8 Simulated pesticide loads for combinations of maximum and minimum sorption and degradation values, together with the simulated load using average inputs and the observed value.

	Avg. K_{oc} Avg. DT_{50}	Max. K_{oc} Max DT_{50}	Max. K_{oc} Min. DT_{50}	Min. K_{oc} Max DT_{50}	Min. K_{oc} Min. DT_{50}	Observed load
			Loads (kg/4 years)			
Chlorotoluron						
SPIDER	8.68	2.33	1.91	30.0	22.5	16.3
MACRO	37.1	14.5	14.1	137	88.5	
MCPA						
SPIDER	0.346	0.230	0.000	9.53	0.036	28.2
MACRO	0.983	1.14	0.002	6.52	0.007	
Clopyralid						
SPIDER	13.0	18.0	9.07	22.8	9.32	19.0
MACRO	0.669	0.878	0.176	1.76	0.183	



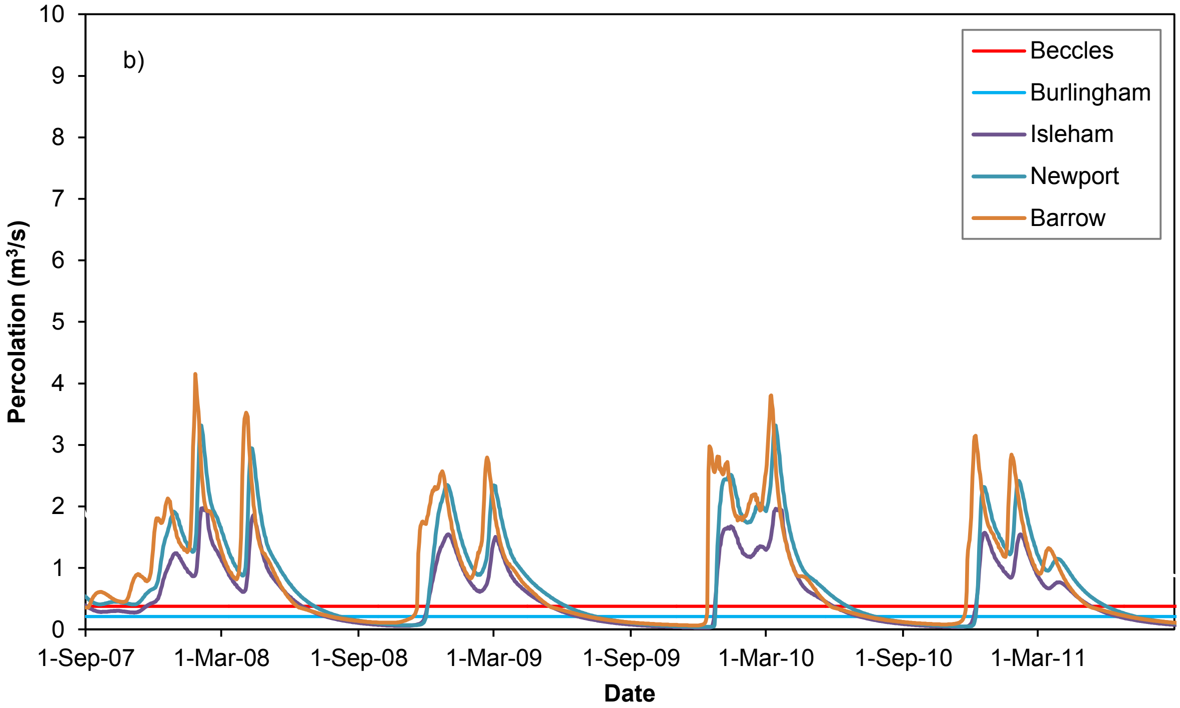
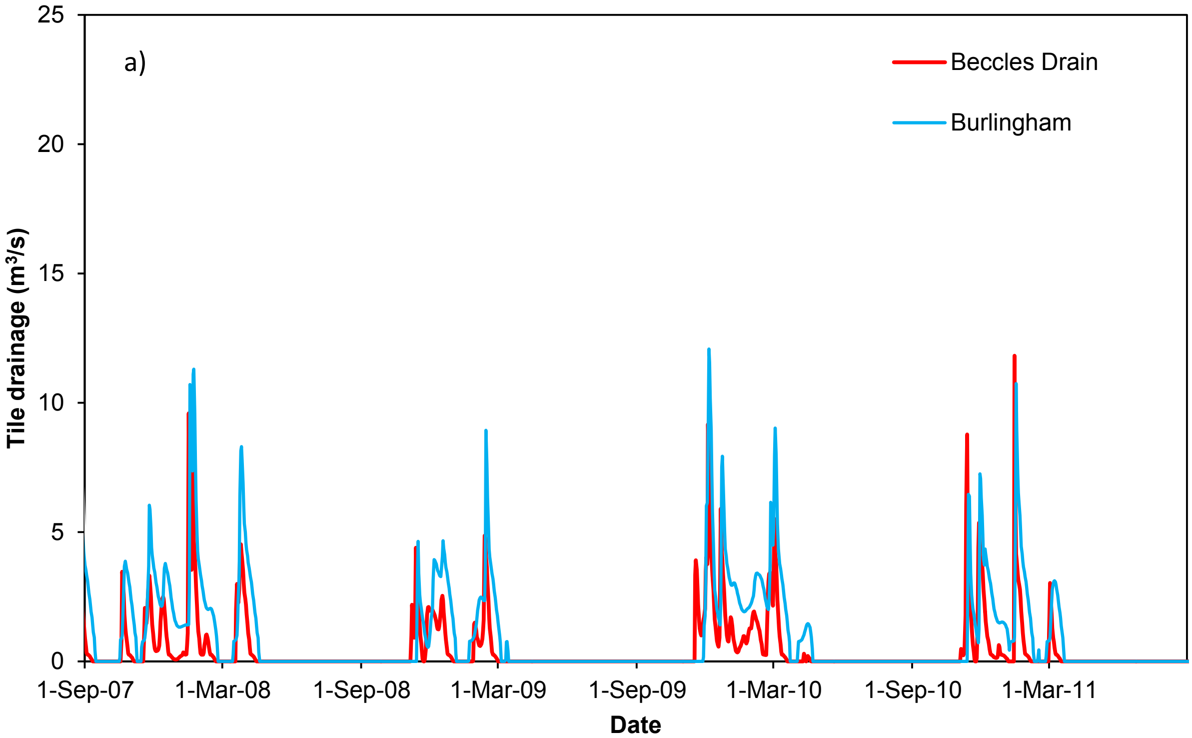
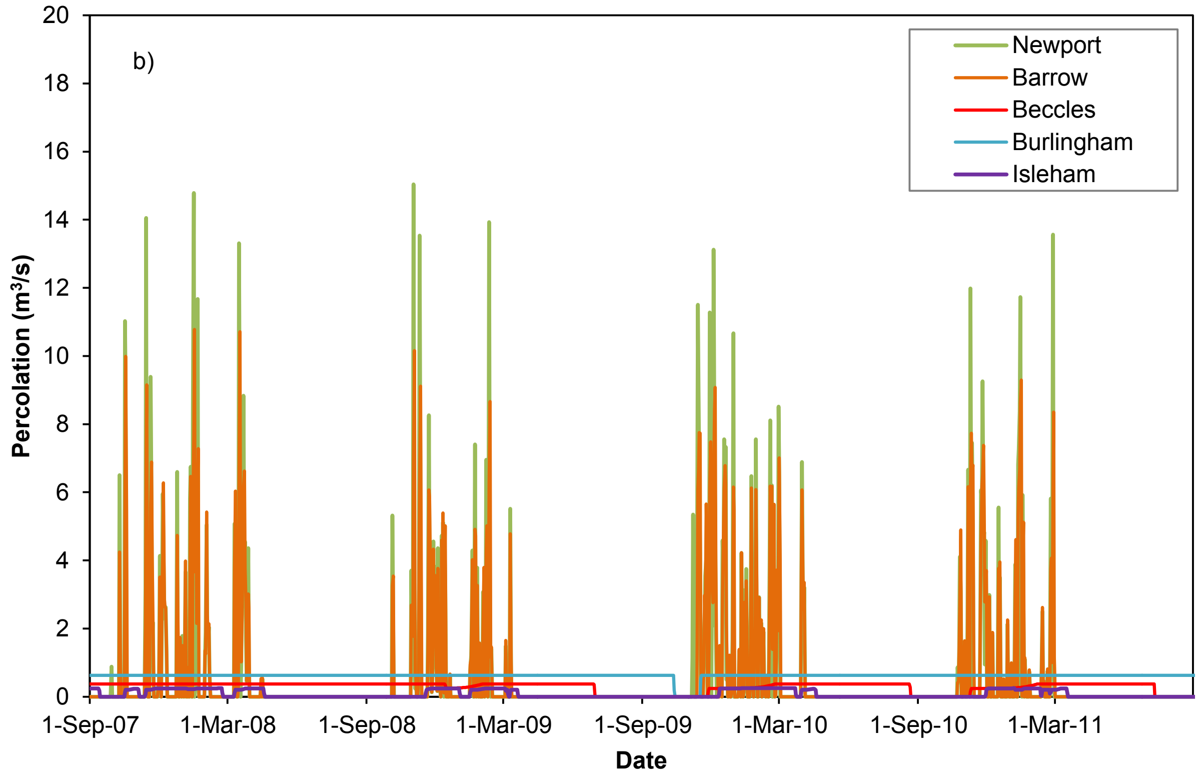


Figure A–8 Hydrographs simulated by MACRO for different soil types for a) drain flow and b) percolation.





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864 **Figure A–9** Hydrographs simulated by SPIDER for different soil types for a) drain flow and b) percolation.